

Application of Neural Networks to a Predictive Extended Corresponding States Model for Pure Halocarbon Thermodynamics ¹

G. Scalabrin ^{2,3}, L. Piazza ², G. Cristofoli ²

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² Dipartimento di Fisica Tecnica, Università di Padova, via Venezia 1 - I-35131 Padova, Italy

³ To whom correspondence should be addressed

ABSTRACT

The Extended Corresponding States (ECS) model has been extensively studied for representing the thermodynamic surface of pure fluids and mixtures in the $a^R(\mathbf{r}, T)$ form and the most advanced version is currently the one for HFC [1], but the shape factors $\mathcal{J}(\mathbf{r}, T)$ and $\mathbf{j}(\mathbf{r}, T)$ have yet to be determined as analytical functions for the whole $P\mathbf{r}T$ surface of a pure fluid.

For a sample of pure halocarbons (HA), this work aims to solve the fundamental problem of determining the individual shape functions on the entire $P\mathbf{r}T$ domain through an innovative predictive procedure using a density model requiring only a single saturated liquid density input. An original algorithm using artificial neural networks (ANNs) enables the determination of the $\mathcal{J}(\mathbf{r}, T)$ and $\mathbf{j}(\mathbf{r}, T)$ functions from *a priori* knowledge of their functional forms. The proposed algorithm focuses on the determination of the residual Helmholtz energy $a^R(\mathbf{r}, T)$ for each fluid, subsequently allowing any other thermodynamic residual function to be calculated through the first and second derivatives of temperature and density. For each fluid studied, the model has been validated for residual functions against the same functions coming from highly accurate DEoS. The prediction accuracies reach AAD values ranging from 0.3 to 7.8%, spanning from vapor and liquid regions to supercritical conditions, while the corresponding results of the ECS method range from 0.54 to 20%.

KEY WORDS: Density, Extended Corresponding States, Feed forward neural networks, Fundamental equation of state, Helmholtz energy equation, Refrigerants, Residual functions.

1. INTRODUCTION

The theoretical background for the Corresponding States is based on a similitude hypothesis of the potential energies for the components of a family of fluids [2,3]. The fluids pertaining to a family meeting this requirement are considered to share a condition of *conformality*, which is intended as a potential energies similitude. This implies the similitude of the $\mathbf{y}(P, \mathbf{r}, T)$ surfaces of each fluid, where P is the pressure, \mathbf{r} the density and T the temperature. Thus, if two fluids i and j pertain to a conformal family, then:

$$\mathbf{y}_i \left[\left(\frac{P}{P_i^c} \right) \left(\frac{V}{V_i^c} \right) \left(\frac{T}{T_i^c} \right) \right] = \mathbf{y}_j \left[\left(\frac{P}{P_j^c} \right) \left(\frac{V}{V_j^c} \right) \left(\frac{T}{T_j^c} \right) \right] = 0 \quad (1)$$

from which it follows that an f function:

$$P_r = f(T_r, V_r) \quad (2)$$

is the same for all the conformal fluids. In eqs. (1,2) V is the volume, while the superscript c and the subscript r indicate the critical and reduced values, respectively.

Then all the derived residual state functions are conformal, too. In particular, it has been demonstrated through further developments of statistical mechanics theory [1,4] that the fundamental conformality condition can be reduced to the following relation:

$$a_j^R(\mathbf{r}_j, T_j) = a_i^R(\mathbf{r}_i, T_i) = a_i^R \left(\frac{\mathbf{r}_j}{\mathbf{r}_j^c} \cdot \mathbf{r}_i^c, \frac{T_j}{T_j^c} \cdot T_i^c \right) \quad (3)$$

where a^R is the residual Helmholtz free energy. It emerged that this relation is not satisfied even for the noble gases and the fluids considered here. A correction to this model is consequently needed, the detail of which is shown later on. Nonetheless, a knowledge of the $\mathbf{y}(P, \mathbf{r}, T)$ surfaces is now available, with the highest possible

accuracy, from DEoS in the form developed following the Schmidt-Wagner technique [6]. The fluids considered in this study are indicated in Table 1, together with the limits of validity of their DEoS. First of all, two grids in the independent T_r , P_r variables were set up with the steps indicated in Table 2 for ANN training and validation, respectively. The training set counts approximately 600 points in all, while the validation set is composed of more than 5000 points. The ranges of T_r and P_r were then selected for each fluid in order to observe the single range of validity for the DEoS, Table 1.

2. ECS IDENTITIES

According to classical ECS theory, two fluids are considered conformal if they obey the following condition:

$$a_j^R(\mathbf{r}_j, T_j) = a_0^R(\mathbf{r}_0, T_0) \quad (4)$$

in which subscripts 0 and j stand for the reference fluid and the fluid of interest, respectively. A DEoS on the $a_0^R(\mathbf{r}_0, T_0)$ form is then needed for the reference fluid.

In a two-parameter Corresponding States framework, the condition of eq. (4) would be satisfied by “distorting” the independent variables through the constant *scale factors* h_j and f_j :

$$T_0 = \frac{T_j}{f_j} \quad f_j = \left(\frac{T_j^c}{T_0^c} \right) \quad \mathbf{r}_0 = \mathbf{r}_j h_j \quad h_j = \left(\frac{\mathbf{r}_0^c}{\mathbf{r}_j^c} \right) \quad (5,6)$$

As already mentioned, this is not sufficient for the real fluids and a further correction to the former “distortion” has to be introduced by means of the shape factors $\mathbf{q}_j(\mathbf{r}_j, T_j)$ and $\mathbf{f}_j(\mathbf{r}_j, T_j)$:

$$f_j = \left(\frac{T_j^c}{T_0^c} \right) \mathbf{q}_j(\mathbf{r}_j, T_j) \quad h_j = \left(\frac{\mathbf{r}_0^c}{\mathbf{r}_j^c} \right) \mathbf{f}_j(\mathbf{r}_j, T_j) \quad (7,8)$$

From the fundamental relation, eq. (4), the formalism to obtain any thermodynamic property can now be developed. Restricting our attention to the more frequently applied thermodynamic functions, the following hold true:

$$Z_j^R = u_0^R F_r + Z_0^R (1 + H_r) \quad (9)$$

$$u_j^R = u_0^R (1 - F_T) - Z_0^R H_T \quad (10)$$

$$s_j^R = s_0^R - u_0^R F_T - Z_0^R H_T \quad (11)$$

$$h_j^R = h_0^R + u_0^R (F_r - F_T) + Z_0^R (H_r - H_T) \quad (12)$$

$$g_j^R = g_0^R + Z_0^R H_r + u_0^R F_r \quad (13)$$

$$\text{with: } F_T = \left(\frac{\partial f_j}{\partial T_j} \right)_{\mathbf{r}_j} \left(\frac{T_j}{f_j} \right) \quad F_r = \left(\frac{\partial f_j}{\partial \mathbf{r}_j} \right)_{T_j} \left(\frac{\mathbf{r}_j}{f_j} \right) \quad (14,15)$$

$$H_T = \left(\frac{\partial h_j}{\partial T_j} \right)_{\mathbf{r}_j} \left(\frac{T_j}{h_j} \right) \quad H_r = \left(\frac{\partial h_j}{\partial \mathbf{r}_j} \right)_{T_j} \left(\frac{\mathbf{r}_j}{h_j} \right) \quad (16,17)$$

3. NEURAL NETWORKS

A new model is proposed here, based on the combination of ECS theory with neural networks (NN). Neural networks are versatile function approximators. We have chosen to represent both of the *shape factors* by means of a single *Multi-Layer Feedforward Network* (MLFN) with 2 outputs, i.e. the *shape factor* functions, eqs. (7,8), since these take effect simultaneously, distorting the independent variables that enter the reference

fluid DEoS, eq. (4). The NN are used here to represent the *shape factors* $\mathbf{J}_j = \mathbf{J}_j(T_j, \mathbf{r}_j)$ and $\mathbf{f}_j = \mathbf{f}_j(T_j, \mathbf{r}_j)$ as functions of the independent variables (T_j, \mathbf{r}_j) .

Fig. 1 shows the general architecture of a three-layer Feedforward Neural Network in which the two values of the input layer, U_1 and U_2 , represent the independent thermodynamic variables, each related to reduced temperature and reduced density. The two values of the output layer, S_1 and S_2 , represent the *shape factors* $\mathbf{J}_j = \mathbf{J}_j(T_j, \mathbf{r}_j)$ and $\mathbf{f}_j = \mathbf{f}_j(T_j, \mathbf{r}_j)$. For the sake of neural network generalization, both input and output values are compressed here within the same range 0.05÷0.95. The transfer function used here is a sigmoid function of the form:

$$f(x) = \mathbf{a} \frac{I}{1 + e^{-2 \mathbf{b} x}} \quad (18)$$

Two parameters have been applied in eq. (18) to make the function's behavior more flexible: \mathbf{a} changes the activation span and \mathbf{b} determines the steepness of the sigmoid function. The neural equation has some parameters set at the following values:

$$\begin{array}{llll} I = 3 & \text{Bias } 1 = 1.0 & A_{min} = 0.05 & \mathbf{a} = 1.0 \\ K = 2 & \text{Bias } 2 = 1.0 & A_{max} = 0.95 & \mathbf{b} = 0.005 \end{array}$$

and its analytical form is:

$$u_i = \frac{A_{max} - A_{min}}{V_{max,i} - V_{min,i}} \quad 1 \leq i \leq I-1 \quad (19)$$

$$s_k = \frac{A_{max} - A_{min}}{W_{max,k} - W_{min,k}} \quad 1 \leq k \leq K \quad (20)$$

$$W_k = \frac{S_k - A_{min}}{S_k} + W_{min,k} \quad 1 \leq k \leq K \quad (21)$$

$$S_k = f \left(\sum_{j=1}^{J+1} w_{jk} H_j \right) \quad 1 \leq k \leq K \quad (22)$$

$$H_j = f\left(\sum_{i=1}^I w_{ij} U_i\right) \quad 1 \leq j \leq J \quad (23)$$

$$H_{J+1} = \text{Bias } 2$$

$$U_i = u_i(V_i - V_{\min,i}) + A_{\min} \quad 1 \leq i \leq I-1 \quad (24)$$

$$U_I = \text{Bias } 1$$

In our case it is:

$$V_1 = T_{r,j} \quad V_2 = \mathbf{d}_j = (\mathbf{r}/\mathbf{r}^c)_j \quad W_1 = \mathbf{J}_j(T_{r,j}, \mathbf{d}_j) \quad W_2 = \mathbf{f}_j(T_{r,j}, \mathbf{d}_j)$$

The following parameters have to be defined according to the specific problem. J is the number of neurons in the hidden layer and, in our case, it was found that 7 was an ideal compromise between computation speed and accuracy of the resulting function. $V_{\min,i}$ and $V_{\max,i}$ are the limits of the independent input variables for the training set; $W_{\min,k}$ and $W_{\max,k}$ are the limit values of the shape factors for their generalization that, in this case, were set between 0.8 and 1.2. Due to the general form of the MLFN selected for application to the present problem, Fig. 1, the NN weighting factors are 21 for the first matrix w_{ij} and 16 for the second matrix w_{jk} , for a total of 37 weighting factors. The values of the weighting factor matrixes, w_{ij} and w_{jk} , are the ECS-NN EoS parameters, i.e. the unknowns of the proposed EoS which have to be obtained individually for each fluid of interest through an optimization procedure [14].

4. MLFN FUNCTION APPROXIMATOR TESTING

First we verified the ability of this model to approximate the fundamental thermodynamic function $a_j^R(T_j, \mathbf{r}_j)$ of one of the fluids considered. We selected R134a as the reference fluid and chose to approximate the $a_j^R(T_j, \mathbf{r}_j)$ DEoS function of R32.

We generated $a_j^R(T_j, \mathbf{r}_j)$ data from the R32 DEoS in vapor, liquid and supercritical zones, as specified in section 2, and then trained the network with said data. The objective function assumed was:

$$f_{ob,1} = \frac{1}{n} \sum_{i=1}^n \left[\frac{(a_j^R)_i^{exp} - (a_j^R)_i^{calc}}{(a_j^R)_i^{exp}} \right]^2 \quad (25)$$

The $a_j^R(T_j, \mathbf{r}_j)$ ECS-NN EoS obtained was tested against the above validation set, demonstrating that the original data were globally approximated with an AAD of less than 0.3 %. on the a^R values. The model can thus approximate the fundamental thermodynamic function $a_j^R(T_j, \mathbf{r}_j)$ to a very good degree, even for the most difficult fluid to represent among those considered here, as explained below.

5. REGRESSION OF A MLFN ON GENERATED DENSITY DATA

Neural *shape factors* can be determined not only from $a_j^R(T_j, \mathbf{r}_j)$ data, but also from any kind of thermodynamic value, providing the appropriate ECS identity is given, e.g. eqs. (4) and eq. (9) through (13). We implemented the regression of \mathbf{PrT} data in the three zones and on the saturation line. We used a DEoS to generate a set of \mathbf{PrT} points in the vapor, liquid and supercritical zones and on the saturation line. This training set counts approximately 600 points in the 3 zones and is described in section 2. For the bulk-phase regression we considered the following objective function:

$$f_{ob,2} = \frac{1}{n} \sum_{i=1}^n \left[\frac{(Z_j^R)_i^{exp} - (Z_j^R)_i^{calc}}{(Z_j^R)_i^{exp}} \right]^2 \quad (26)$$

where $(Z_j^R)^{calc}$ is given by eq. (9), while at saturation a second objective function was considered:

$$f_{ob,3} = \frac{1}{n} \sum_{i=1}^n \left[(\ln \mathbf{j}_j)_i^{sl} - (\ln \mathbf{j}_j)_i^{sv} \right]^2 \quad (27)$$

where $\ln \mathbf{j}_j$ is given by eq. (28) combined with eq. (13):

$$\ln \mathbf{j} = g^R - \ln Z \quad (28)$$

The EoS parameter optimization process was developed using an overall objective function which was selected as a linear combination of the two former functions, eqs. (26,27):

$$f_{ob,overall} = 0.9 \cdot f_{ob,2} + 0.1 \cdot f_{ob,3} \quad (29)$$

After training the network, we tested the model's ability to reproduce the fundamental thermodynamic function $a_j^R(T_j, \mathbf{r}_j)$, and its first partial derivatives related to $Z_j^R(T_j, \mathbf{r}_j)$ and $u_j^R(T_j, \mathbf{r}_j)$. The results are shown in Table 3. Looking at the case of R32, which was formerly studied for the $a_j^R(T_j, \mathbf{r}_j)$ function approximation, its weighted average error deviation for the three zones was 0.4. This figure is only slightly higher than the 0.3 of the former case, so the ECS-NN EoS can be trained on a derived quantity, such as density, without any substantial loss of accuracy on the fundamental surface $a_j^R(T_j, \mathbf{r}_j)$. The u^R function, which is related to a^R through the temperature first derivative of the shape factors, eqs. (10,14,16), can also be represented well.

We then tested the model for the prediction of $Z_j(T_j, P_j)$, $a_j^R(T_j, P_j)$, $u_j^R(T_j, P_j)$, $h_j^R(T_j, P_j)$, $s_j^R(T_j, P_j)$, $g_j^R(T_j, P_j)$ and $\ln \mathbf{j}_j(T_j, P_j)$. An inversion is always needed for practical uses, due to the default choice of T, P as independent variables. The different

choice of independent variables in this second case demands an iterative procedure to find a solution for $\mathbf{r}_j(T_j, P_j)$. The results of the validation study are shown in Table 4. The model volumetric accuracy can be evaluated through the $Z_j(T_j, P_j)$ function; the AAD achieved is comparable with the corresponding value of a Schmidt-Wagner multiparameter DEoS. The residual functions are also well represented, with s^R deviating in the vapor phase at a maximum of 4.15% with respect to a DEoS, whose error deviation for this function (and for some others) is unknown. It is worth emphasizing that the upper limit of the liquid phase was globally less than 1%.

Finally, as proof of its consistency, saturation pressures and saturated liquid and vapor densities were calculated from the model through the VLE condition $\mathbf{j}_{sl} = \mathbf{j}_{sv}$ on the saturation line. The results are presented in Table 5. These three values have to be considered as the residual deviation errors for the final EoS, because all three were used in the minimization objective function.

6. REGRESSION OF A MLFN ON DATA FROM A PREDICTIVE VOLUMETRIC MODEL

In this case, the ECS-NN EoS is trained on density data generated with a volumetric model previously developed by the Authors [15,16,17]. The volumetric model enables the predictive generation of approximate $P\mathbf{r}T$ data, on which our ECS model was subsequently trained. Since the volumetric model needs no more than one experimental saturated liquid density value, the great advantage of this approach is predictivity. The method for developing this model is quite similar to the one described in the former case for “exact” density data. As reference fluids R12 and R134a were selected.

We compared the performance of our ECS-NN model, trained on data generated from the density model, with that of the Huber-Ely ECS model [1]. Both models aim for predictivity, though the latter also requires a saturated liquid volume correlation.

The validation results for our model are shown in Table 6. Because the density data used to train the model are less accurate than in the previous case, a certain drop in precision with respect to the former case is inevitable. This is evident for the supercritical zone in general and particularly for R32, which is always the most difficult fluid to reproduce. The volumetric precision is very good in vapor and liquid phases, with average AAD lower than 0.3 and 0.6 % respectively, but in the supercritical zone it rises over 2.5 %. Generally speaking, the results obtained for the various residual potential functions vary from fluid to fluid and also from one zone to another. The functions' AAD in the liquid zone are around 1 %, while the AAD for the supercritical and vapor zones come between 1 % and 4 %, with only one case exceeding said values, i.e. s^R in the vapor phase, where an AAD of 7.8 % is reached. The validation results of the ECS-NN model on the saturation line are shown in Tab. 7; also in this case the prediction accuracy is worse with error deviations about two times greater. The validation of the Huber-Ely [1] ECS model is shown in Tab. 8. The AAD on P_rT data is around 0.5 % for the liquid, and less than 1.5 % for vapor and supercritical zones. The residual potential functions AAD in the liquid zone are usually below 1.5 %, while the AAD of the vapour phase are significantly greater, generally between 8 and 15 %, with the highest value, for s^R , reaching nearly 20 % as mean value. In the supercritical zone the AAD values are usually limited to 5 % at maximum. Results of the validation test along the saturation line are shown in Tab. 9; the results for density are in particular worse.

7. CONCLUSIONS

A new method for determining shape factors in the Extended Corresponding States modelling framework is proposed. The approach requires an *a priori* analytical form for the shape factor functions and for this the Artificial Neural Networks (ANN), as very versatile function approximators, have been applied. The shape factors are represented through ANN as functions of the two independent variables temperature and density. The ECS-NN EoS parameters are determined through a minimisation procedure. A number of halogenated alkanes for which DEoS are presently available was assumed for the study. The ECS-NN EoS capability in representing P_rT data in vapor, liquid and supercritical zones was verified with an AAD between 0.026 and 0.5 %, which is comparable to the analogous value of a multiparameters DEoS. The accuracy of the model, trained on P_rT data, in representing residual potential functions was also tested obtaining AAD values generally less than 0.8 % for liquid and less than 4 % for vapor and supercritical zones. The ECS-NN EoS has been afterwards trained on P_rT data generated through an original predictive volumetric model requiring a single saturated liquid density value as input for each interest fluid. This makes the whole method predictive, although with an expected slight decrease of accuracy. The AAD values on P_rT data are well less than 1 % in liquid and vapor, while in the supercritical zone they reach 2.5 %. The AAD on residual potential functions are often under 1% for liquid and generally under 4 % for vapor and supercritical zone. The comparison of the present predictive ECS-NN model with the Huber-Ely one [1] shows that in the liquid and supercritical zones the results are comparable, though not uniform for the second model, while the second model presents a marked worsening in the representation of the vapor zone residual potential functions.

The proposed model allows then to predictively obtain an ECS model, with locally defined individual shape factors, which shows a good and equilibrated performance.

REFERENCES

1. M. Huber M., J.F. Ely, *Int. J. Refrig.*, **17**:18 (1994).
2. T.M. Reed, K.E. Gubbins, *Applied Statistical Mechanics*, (McGraw-Hill, New York, 1973).
3. J.S. Rowlinson, F.L. Swinton, *Liquids and Liquid Mixtures*, (Butterworth, Oxford, 1982).
4. J.S. Rowlinson, I.D. Watson, *Chem. Eng. Sci.*, **24**: 1565 (1969).
5. J.F. Ely, *Adv. Cryog. Eng.*, **35**: 1511 (1990).
6. R. Schmidt, W. Wagner, *Fluid Phase Equilibria*, **19**:175 (1985).
7. R.T. Jacobsen, S.G. Penoncello, E.W. Lemmon, *Fluid Phase Equilibria*, **80**: 45 (1992).
8. S.G. Penoncello, R.T. Jacobsen, E.W. Lemmon, *Fluid Phase Equilibria*, **80**: 57 (1992).
9. A. Kamei, S.W. Beyerlein, E.W. Lemmon, *Fluid Phase Equilibria*, **80**: 71 (1992).
10. S.L. Outcalt, M.O. McLinden, *Int. J Thermophys.*, **16**: 79 (1995).
11. S.G. Penoncello, R.T. Jacobsen, K.M. de Reuck, A.E. Elhassan, R.C. Williams, E.W. Lemmon, *Int. J Thermophys.*, **16**: 781 (1995).
12. R. Tillner-Roth, H.D. Baehr, *J. Phys. Chem. Ref. Data*, **23**, 5: 657 (1994).
13. R. Tillner-Roth, *Int. J Thermophys.*, **16**: 91 (1995).
14. J.L. McClelland, D. Rumelhart, *Explorations in parallel distributed processing*, 2 voll., (MIT Press, Cambridge, Massachusetts, 1988).

15. M. Grigante, G. Scalabrin, S. Bobbo, Proc. 20th Int. Cong. of Refrigeration, 19 - 24 Sept. 1999, Sydney (Australia).
16. G. Cristofoli, M. Grigante, G. Scalabrin, *Fluid Phase Equilibria*, in press, (2000).
17. G. Scalabrin, M. Grigante, submitted to: *Int. J. Refrig.*, (2000).

Table 1: Dedicated equations of state (DEoS) and range of validity for the HA fluids considered.

Fluid	Formula	T_r min.	T_r max	P_r max	Ref.
R11	CCl_3F	0.34	1.33	6.8	[7]
R12	CCl_2F_2	0.45	1.56	17.0	[8]
R22	CHClF_2	0.31	1.49	12.0	[9]
R32	CH_2F_2	0.45	1.43	10.3	[10]
R123	CHCl_2CF_3	0.36	1.15	10.9	[11]
R125	CHF_2CF_3	0.51	1.47	18.7	[10]
R134a	CH_2FCF_3	0.45	1.34	17.3	[12]
R152a	CH_3CHF_2	0.40	1.13	6.7	[13]

Table 2: Training and validation grid steps for T_r and P_r .

		Vapor	Liquid	Supercrit.
T_r step	training	0.02	0.02	0.02
	validation	0.01	0.01	0.01
P_r step	training	0.05	0.5	0.5
	validation	0.01	0.1	0.1

Table 3: Residual functions prediction accuracy without inversion for ECS-NN trained on data generated from DEoS.

Property	Fluid	AAD %		
		vapor	liquid	supercrit.
a^R	R11	0.967	0.157	1.593
	R22	0.445	0.054	0.456
	R32	1.071	0.088	0.383
	R123	0.520	0.236	0.197
	R125	0.603	0.237	2.032
	R152a	0.935	0.142	0.525
	avg	0.757	0.151	0.982
Z^R	R11	1.395	0.429	2.069
	R22	0.817	0.258	1.444
	R32	0.980	0.223	1.431
	R123	0.849	0.287	0.986
	R125	0.958	0.371	1.772
	R152a	0.983	0.321	0.950
	avg	1.000	0.315	1.555
u^R	R11	3.474	0.619	2.867
	R22	2.220	0.238	0.662
	R32	2.309	0.328	1.577
	R123	1.726	0.482	0.589
	R125	3.488	0.465	4.709
	R152a	2.179	0.259	0.2943
	avg	2.571	0.398	2.103
Overall		1.443	0.288	1.547

Table 4. Residual functions prediction accuracy with inversion for ECS-NN trained on data generated from DeoS.

	Z			a^R			u^R			h^R			s^R			g^R			$\ln j$		
Fluid	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.
R11	0.27	0.05	0.41	1.28	0.14	1.83	3.72	0.65	2.83	2.87	0.60	1.99	5.89	1.22	5.02	1.29	0.12	1.38	1.06	0.54	1.81
R22	0.11	0.03	0.20	0.55	0.05	0.56	2.32	0.25	0.65	1.83	0.23	0.47	3.57	0.46	1.19	0.59	0.04	0.43	0.48	0.26	0.52
R32	0.37	0.14	0.37	1.33	0.13	0.52	2.64	0.36	1.75	2.25	0.33	1.38	3.49	0.63	2.71	1.25	0.11	0.53	1.15	0.26	0.42
R123	0.18	0.03	0.38	0.69	0.24	0.43	1.90	0.49	0.83	1.57	0.45	0.72	2.69	0.82	1.12	0.71	0.16	0.38	0.58	0.73	0.25
R125	0.20	0.03	0.39	0.75	0.23	2.07	3.62	0.45	4.81	2.72	0.42	3.37	5.94	0.78	9.65	0.74	0.19	1.49	0.65	0.44	2.22
R152a	0.35	0.05	0.50	1.21	0.14	0.74	2.41	0.28	0.48	2.03	0.26	0.47	3.15	0.58	0.51	1.18	0.11	0.62	1.01	0.24	0.69
Avg	0.24	0.06	0.36	0.97	0.15	1.13	2.78	0.41	2.19	2.21	0.38	1.59	4.15	0.75	3.98	0.96	0.12	0.88	0.82	0.41	1.11

Table 6. Residual functions prediction accuracy with inversion for ECS-NN trained on data generated from density model.

	Z			a^R			u^R			h^R			s^R			g^R			$\ln j$		
Fluid	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.
R11	0.18	0.22	0.85	0.97	0.41	1.55	4.80	0.71	2.37	3.60	0.66	1.93	8.17	1.31	3.79	1.04	0.35	1.48	0.88	1.44	1.36
R22	0.15	0.18	0.78	0.49	0.08	1.08	1.69	0.27	0.55	1.25	0.25	0.41	2.96	0.46	1.33	0.49	0.09	1.18	0.43	0.48	0.44
R32	0.85	1.59	7.31	3.08	1.26	12.3	10.5	2.96	3.83	7.75	2.63	4.61	17.1	5.98	5.18	3.23	1.07	11.7	2.59	2.00	10.0
R123	0.12	0.30	0.80	0.80	0.27	0.85	3.08	0.42	0.64	2.45	0.39	0.62	4.60	0.83	0.73	0.81	0.25	0.82	0.74	0.95	0.51
R125	0.15	0.36	2.04	1.79	0.39	3.44	3.20	0.69	5.31	2.37	0.61	4.24	5.45	1.29	9.67	1.62	0.35	3.53	1.78	0.63	2.79
R152a	0.33	0.70	2.60	1.94	0.50	2.74	6.02	0.96	1.51	4.85	0.87	1.34	8.49	1.72	2.41	1.91	0.41	2.53	1.78	0.62	1.76
Avg	0.27	0.56	2.55	1.50	0.49	4.10	4.87	1.00	2.67	3.70	0.90	2.47	7.77	1.93	4.38	1.50	0.42	3.98	1.36	1.02	3.21

Table 8. Residual functions prediction accuracy of the conventional ECS model (Huber-Ely, 1994).

	Z			a^R			u^R			h^R			s^R			g^R			$\ln j$		
Fluid	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.	vap.	liq.	sup.
R11	1.67	0.65	1.13	12.5	0.96	2.95	23.3	1.40	3.46	19.5	1.32	3.07	32.6	2.75	4.41	11.9	0.87	2.64	11.6	2.92	2.99
R22	0.75	0.21	0.45	5.31	0.32	0.97	8.91	0.64	1.78	7.61	0.60	1.46	11.4	1.17	2.36	5.06	0.29	0.90	4.91	1.36	1.03
R32	2.57	0.96	2.40	14.7	1.02	6.19	20.3	1.02	7.07	18.6	0.89	6.49	23.8	2.67	8.62	14.1	0.92	5.57	13.6	1.56	5.81
R123	0.80	0.51	0.81	14.7	1.02	6.19	10.8	0.73	2.71	9.10	0.69	2.16	14.2	1.28	3.70	5.36	0.46	1.15	5.10	1.33	1.10
R125	0.91	0.50	1.19	5.30	0.46	2.50	15.8	0.90	7.99	12.6	0.84	5.82	23.5	1.60	14.9	5.28	0.45	2.23	4.72	0.72	1.67
R152a	1.14	0.45	0.92	7.03	0.70	1.69	10.5	1.35	1.85	9.47	1.25	1.76	12.7	1.97	2.18	6.72	0.59	1.49	6.51	1.45	1.90
Avg	1.14	0.45	0.92	8.41	0.66	2.85	14.1	1.01	4.59	12.8	0.93	3.82	19.8	1.91	6.78	8.07	0.60	2.57	7.75	1.56	2.84

Table 5. Prediction accuracy at saturation for ECS-NN trained on data from DEoS.

Fluid	Sat. vap. pressure	Sat. liq. density	Sat. vap. density
R11	0.650	0.189	1.162
R22	0.239	0.098	0.700
R32	0.432	1.155	1.392
R123	0.865	0.120	1.415
R125	0.993	0.147	1.155
R152a	0.651	0.536	1.203
Avg	0.638	0.374	1.171

Table 7. Prediction accuracy at saturation for ECS-NN trained on data from density model.

Fluid	Sat. vap. pressure	Sat. liq. density	Sat. vap. density
R11	1.086	1.876	1.716
R22	0.341	0.212	0.674
R32	2.984	0.312	4.728
R123	0.869	0.128	1.381
R125	1.34	0.144	1.890
R152a	1.351	0.733	2.109
Avg	1.325	0.567	2.083

Table 9. Prediction accuracy at saturation for conventional ECS model (Huber-Ely, 1994).

Fluid	Sat. vap. pressure	Sat. liq. density	Sat. vap. density
R11	1.079	3.355	5.418
R22	0.647	2.384	4.064
R32	0.661	4.438	7.445
R123	0.701	2.835	4.739
R125	1.705	2.407	3.151
R152a	3.032	3.643	7.54
Avg	1.304	3.177	5.392

Figure captions

Fig. 1. Three layers Feed-Forward Neural Network architecture.

Fig. 2. Percent error deviation on $a_j^R(\mathbf{t}_j, \mathbf{d}_j)$ for the interest fluid R152a. ECS-NN model trained on data generated from DEoS.

Fig. 3. Shape factor $\mathbf{J}_j = \mathbf{J}_j(\mathbf{t}_j, \mathbf{d}_j)$ for the interest fluid R152a. ECS-NN model trained on data generated from DEoS.

Fig. 4. Shape factor $\mathbf{f}_j = \mathbf{f}_j(\mathbf{t}_j, \mathbf{d}_j)$ for the interest fluid R152a. ECS-NN model trained on data generated from DEoS.







